

Methods and data processing report for compositional characterization of size-fractionated particles from large volume filtration using in-situ pumps during EXPORTSNP

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In-situ pump deployment and sample collection

To understand the sources and fate of carbon associated with the biological pump, sampling of particles is needed. To collect enough material to obtain relevant data on the concentrations of carbon and associated elements on the rarer, larger suspended particles, in-situ pumping is commonly used to filter upwards of 1000 L. We deployed battery powered in-situ pumps (McLane Industries) whereby water entering the pump passed first through two screens (51 μm followed by 5 μm nominal pore size) followed by a 1 μm nominal pore-size QMA (quartz based) filter (all were 142 mm diameter). Collected size-fractionated particles were analyzed for **thorium-234**, **particulate carbon (PC)**, **particulate inorganic carbon (PIC)**, **particulate nitrogen (PN)** and **biogenic silica (bSi)**. A subset of samples was also analyzed for **phosphorus**, **barium**, **Ba isotopic composition**, **polonium-210** and **lead-210**. Further subsamples were shared with other PI's for organic isotopes (Hilary Close, University of Miami; Brian Popp, University of Hawaii) and HPLC (Collin Roesler, Bowdoin College). A second filter holder was attached to each in-situ pump containing a 51 μm screen followed by a 0.8 μm nominal pore-size SUPOR filter (also 142 mm diameter) for trace metal (Phoebe Lam, University of California) and further organic isotope (H. Close, B. Popp) measurements.

In-situ pumps were programmed to pump for 4-5 hours and starting flow rate was set at 8 L/min. The volumes pumped ranged from 700 to 1500 L depending on particle loading and voltage drop. The QMA's were subsampled with "punches" of varying size for the different analytes as particle distribution is even across the filter (Lam et al. 2015). Swimmers observed by naked eye were picked from 51 μm screens. Particles were gently rinsed off the screens on to 25 mm diameter 1 μm pore size silver filters that were dried and beta counted at sea for ^{234}Th , and subsequently recounted on shore for ^{234}Th prior to splitting by weight into subfractions for PC, PN, PIC and bSi (Lamborg et al. 2008). As in GEOTRACES, the screens were cut into "pizza" wedges for ^{234}Th , ^{210}Po - ^{210}Pb and Ba analysis (only at 3 stations). Given the sampling of 6 depths (5 trap depths plus 50 m) at 12 stations, this generated 72 samples for each of the three size classes. We had process blanks for each filter type: screens (51 and 5 μm) and QMA filters were loaded in a filter holder that was deployed on the deepest pump (500 m) three times during the cruise. Samples were generally dried, except for a subset of QMA punches for phosphorus and samples for HPLC (C. Roesler) and organic isotopes (H. Close, B. Popp).

Sample analysis

^{234}Th was counted by beta spectrometry first at sea and six months later at WHOI to quantify the background activity of high-energy beta emitters.

PC and PN were analyzed using a high-temperature combustion technique on a Thermo Electron FlashEA 1112 C/N analyzer. **PIC** was determined by coulometric analysis of CO_2 after acidifying the subsamples with phosphoric acid.

To determine **bSi** content, filters were extracted in 0.2 M NaOH for 1 hour at 95°C and then neutralized with 1 M HCl. Subsamples were analyzed for dissolved silicate on the same day following standard spectrophotometric methods (Strickland and Parsons, 1972). bSi was not determined from the quartz-based QMA filter but from the SUPOR filter used in the second filter holder.

Filter subsections for **Ba and P** analysis were leached with 0.6 M hydrochloric acid at 60°C for ~16 hours (Bishop and Wood, 2008; Bishop et al., 2012). Leachates were diluted with 2% nitric acid, doped to an indium concentration of ~1 ng/mL, and analyzed for multi-element concentrations using a Thermo Scientific iCAP quadrupole inductively-coupled plasma mass spectrometer (ICP-MS) situated at the WHOI Plasma Facility. Quantification of barium and

phosphorus was achieved via comparison of sample ion beam intensities to those of reference solutions with known concentrations. Samples containing sufficient material for Ba-isotopic analysis were aliquoted, spiked with a ^{135}Ba - ^{136}Ba double spike, and Ba purified from the sample matrix using two passes of ion-exchange chromatography. Analyses were performed using a ThermoFisher Neptune multi-collector ICP-MS, also situated at the WHOI Plasma Facility.

The subsamples for ^{210}Po and ^{210}Pb were digested right after the cruise at Universitat Autònoma de Barcelona (UAB, Spain) using a mixture of concentrated HNO_3 , HF and HCl and reconstructed to 1 M HCl. Lead and polonium were separated by auto-deposition of Po onto silver discs. i.e. plating (Flynn 1968) which were then counted by alpha spectrometry (Fleer and Bacon, 1984). Solutions were re-plated and passed through anion-exchange resin to ensure the complete elimination of Po from samples (Rigaud et al., 2013). Samples were plated again after six months for determination of ^{210}Pb via ^{210}Po ingrowth.

Parameters measured in size-fractionated (>1-5; 5-51; >51 μm) particles and units

Parameter	SeaBASS name	Units
Thorium-234	conc_Th_234	dpm/L
Particulate carbon	PC	mmol/m ³
Particulate inorganic carbon	PIC	mol/m ³
Particulate nitrogen	PN_mmol	mmol/m ³
*Biogenic silica	bSi	mmol/m ³
Phosphorus	PTP	mmol/m ³
Barium	conc_Ba_total	nmol/L
Ba-isotopic composition ($\delta^{138/134}\text{Ba}_{\text{NIST}}$)	Ba_138_134_d_delta	per mil
Polonium-210	conc_Po_210	dpm/L
Lead-210	conc_Pb_210	dpm/L

*bSi was measured in SUPOR filters instead of QMA. Size-fractionated particles for bSi are >0.8-51; 5-51; >51 μm

Uncertainties and quality control

For all parameters, the average of the process blanks was subtracted from each measurement before dividing by the filtered volume. Data for each parameter have an associated uncertainty from blank correction (standard deviation), the weighing error of the analytical balance used for splitting filters, and counting (^{234}Th , ^{210}Po and ^{210}Pb). The uncertainties associated with ^{210}Pb and ^{210}Po measurements were quantified following Rigaud et al. (2013). 2 SD uncertainties are reported for Ba-isotopic measurements. Barium data accuracy was monitored via processing and analysis of international reference materials as part of each batch of samples. Extraneous Ba added during sample processing was monitored via processing and analyzing of sub-ng aliquots of an isotopic double spike (^{135}Ba – ^{136}Ba) through all sample purification procedures.

High $\text{PC}/^{234}\text{Th}$ ratios are indicative of possible swimmer contamination (Buesseler, et al., 2007) on the largest particle size fraction (>51 μm). Outliers are identified as measurements whose value is greater than the third quartile by more than 1.5 times the interquartile range (third quartile-first quartile) in a box plot. 7 outliers have been flagged in the dataset since particulate carbon, nitrogen and phosphorus concentrations on >51 μm particles may be artificially high due to the presence of swimmers.

Key analytical method references

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